

Influence of Alloying on the Thermal Stability of Model Heat Resistant Compositions

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Abstract. We studied the phase transformations at high temperatures in the carbonless heat-resistant nickel alloys by the differential thermal analysis and we calculated their thermal stability. For a relatively low alloyed compositions the greatest positive effect is achieved when it were alloyed by γ' -forming elements such as the niobium and titanium. The greatest thermal stability at temperatures below 1100°C is achieved for these alloys in the low alloyed composition. Multi-component carbonless heat resistant nickel alloys have the best characteristics when compositions contain the rhenium and a small amount of the tantalum. However, the most thermal stability at temperatures up to 1200°C has a composition that includes only 6% of tantalum.

1. Introduction

Foundry heat-resistant nickel alloys are intended for the manufacture of the most critical parts of turboshaft engines – the turbine blades that operating at high temperatures in an aggressive environment. Improving turboshaft engines, increasing their power, reliability and durability requires the development of new complex-alloyed compositions.

One of the important parameters is structure thermal stability information which is needed to create new highly effective compositions, assess the performance of alloys that are operated at extremely high temperatures [1, 2]. Thermostability of high-temperature nickel alloys is determined by the temperatures of the beginning and end of the dissolution of the secondary intermetallic γ' -phase – $t_{b.d.}$ and t_{solv} , by the kinetics of dissolution of the secondary γ' -phase in the temperature interval $t_{b.d.} - t_{solv}$, as well as the temperature of the solidus t_s . Temperature t_{solv} limits the region of the alloy existence in the form of a matrix that is strengthened by the secondary intermetallic γ' -phase embedded in it, and t_s is the temperature range for the alloy existence as a structural material.

Technological operations for turboshaft engines critical parts production from the majority of high-temperature nickel alloys are required thermal treatment. It includes homogenization operations, i.e. heating in the interval $t_{solv} - t_s$ with prolonged exposure to 2-3 hours, hardening and subsequent aging. In this regard, the expansion temperature range $t_{solv} - t_s$ allows to optimize the homogenization mode. For products obtained by foundry methods, temperatures of solidus t_s and liquidus t_L are important parameters for choosing optimal melting and casting temperatures, which significantly affects both the emerging structure and properties of parts and the output of the finished product [1].

2. Materials and methods

The most promising obtaining products method for modern turboshaft engines is single-crystal casting, which allows to get rid of grain boundaries and significantly increase operating temperatures



[2]. It is established [3] that carbon-free nickel refractory alloys possess the most favorable complex of structure and properties. In this case, the temperatures of phase transformations in some model carbon-free high-temperature alloys have been studied. Their chemical composition is given in Table 1.

Table 1. The studied chemical composition of the model high-temperature nickel alloys.

Sample №	The content of alloying elements, % mass.										
	Ni	Co	Cr	Al	W	Mo	Ti	Nb	Hf	Ta	Re
1	Base	5.00	4.50	6.56	8.95	-	-	-	-	-	-
2	Base	5.00	4.50	6.56	8.95	-	1.00	-	-	-	-
3	Base	5.00	4.50	6.56	8.95	-	-	1.00	-	-	-
4	Base	5.00	4.50	6.56	8.95	-	-	-	-	4.00	-
5	Base	5.00	4.50	6.56	8.95	-	-	-	-	2.00	4.00
6	Base	7.65	5.05	6.28	8.03	0.36	0.31	0.86	0.21	3.60	-
7	Base	7.65	5.05	6.28	10.00	0.36	0.31	0.86	0.21	3.60	-
8	Base	7.65	5.05	6.28	8.00	0.36	0.31	0.86	0.21	6.00	-
9	Base	7.65	5.05	6.28	8.00	0.36	0.31	0.86	0.21	4.00	2.00
10	Base	7.65	5.05	6.28	8.00	0.36	0.31	0.86	0.21	6.00	2.00
11	Base	7.65	7.05	6.28	8.00	0.36	0.31	0.86	0.21	6.00	-

The phase transformations temperatures are most often determined by the methods of thermal and differential-thermal analysis, the kinetics of dissolution of the secondary Z-phase is studied both by dilatometric methods and by high-temperature metallography methods.

The characteristic transformation temperatures in the studied carbon-free nickel alloys were detected on the VDTA-8M unit with monotonic heating and cooling of the thermographic block with speed of 20° C/min [4].

3. Results and discussions

Qualitative metallographic analysis makes it possible to reveal the structure of cast samples. After etching, the dendrites axes of the first and second order have a light color, the interdendritic space is colored dark, the eutectic of the globular morphology based on the intermetallic phase is white (figure 1). Both in the dendrites axes and in the inter-axial space, fine-grained inclusions of the secondary γ' -phase are visible. The secondary γ' -phase is distributed evenly, but in the interdendritic space its displacements are larger.

Analysis of the obtained DTA curves, published data [5-8], and the results of qualitative metallographic analysis makes it possible to identify the phase transformations founded during the research. The following phase transformations were revealed during heating and their temperatures were determined:

1. Particles dissolution of secondary γ' -phase in a metal matrix - doped γ -solid solution (t_{solv}).
2. The beginning of the alloy most fusible constituent melting - the eutectic on the basis of γ and γ' -phase (t_s).

3. The end of eutectic melting and the beginning of the metal matrix melting. Unfortunately, it is difficult to separate the heat effects associated with each of these processes on the DTA curves, so the temperature of these transformations was not taken into account in the results analyses.

4. Complete melting of the sample (t_L).



Figure 1. The structure of the cast carbonless superalloy.

The temperatures of complete dissolution of the secondary γ' -phase (t_{solv}), solidus (t_S), liquidus (t_L) determined from the DTA curves were used to calculate the melting temperature intervals ($t_L - t_S$), the existence of a doped solid solution ($t_S - t_{\text{solv}}$). Based on the liquidus temperatures during heating and cooling data, the supercooling of the melt was determined $\Delta T = t_{L\text{heat}} - t_{L\text{cool}}$ (Table 2).

Table 2. Temperatures and intervals of phase transformations.

№ Sample	$T_{L\text{heat}},$ $^{\circ}\text{C}$	$T_S,$ $^{\circ}\text{C}$	$T_{\text{solv}},$ $^{\circ}\text{C}$	$T_{b.d.},$ $^{\circ}\text{C}$	$T_L - T_S,$ $^{\circ}\text{C}$	$T_S - T_{\text{solv}},$ $^{\circ}\text{C}$	$T_{L\text{cool}},$ $^{\circ}\text{C}$	$\Delta T,$ $^{\circ}\text{C}$
1	1480	1270	1260	780	210	10	1400	80
2	1480	1290	1275	725	190	15	1425	55
3	1475	1315	1265	685	160	50	1435	40
4	1465	1305	1250	675	160	55	1415	50
5	1470	1295	1245	740	175	50	1425	45
6	1455	1325	1270	775	120	55	1390	55
7	1455	1285	1250	770	175	35	1405	50
8	1440	1295	1280	820	145	15	1410	30
9	1440	1340	1275	715	100	65	1395	45
10	1445	1325	1265	730	120	60	1380	65
11	1455	1330	1260	670	125	70	1390	65

When a low-base base composition (composition 1) is added to 1 % mass. of titanium or niobium temperature t_{solv} , t_S is increased, the interval $t_S - t_{\text{solv}}$ is widened, and the supercooling during the crystallization of the melt decreased.

The addition of tantalum and rhenium to the base composition leads to an increase in the solidus temperature, to a certain decrease in the temperature of complete dissolution of the secondary γ' -phase, to the expansion of the temperature interval $t_S - t_{\text{solv}}$, decrease of the melting interval and supercooling of the melt.

Thus, for the first series of samples characterized by a relatively low level of doping, the most favorable effect is exerted by elements that increase the thermal stability of the γ' -phase-titanium and niobium. Moreover, if high-temperature heat treatment (homogenization and subsequent aging) is not

planned for the studied compositions, the best effect is obtained by alloying the base alloy with titanium. In this case, the dissolution temperature t_{solv} of the secondary γ' -phase is substantially increased, but the interval between the t_{solv} and the solidus temperature t_s is negligible.

If heat treatment is provided for the alloy, niobium alloying is most effective. For such an alloy, in comparison with other compositions, the thermostability of the alloy increases (increases t_{solv}) and the interval between t_{solv} and the temperature of the solidus is significantly increased.

The introduction of low-alloyed carbon-free nickel alloys of tantalum and rhenium does not increase their thermal stability, so it is ineffective.

Complex alloying of alloy 1, i.e. the introduction of niobium, titanium, hafnium and tantalum into it leads to a sharp increase in the temperatures of complete dissolution of the secondary γ' -phase and solidus. At the same time interval $t_s - t_{\text{solv}}$ increased to 55°C, the melting interval as a result of growth of t_s and decrease of t_L decreased to 120°C.

Further, the effect of alloying components on the temperature of phase transformations in complex-alloyed alloys (compositions 6-11) was studied. It turned out that the introduction of tungsten or tantalum into the alloy leads to a decrease in the solidus temperature and, as a consequence, to a significant narrowing of the interval $t_s - t_{\text{solv}}$ region of existence of a homogeneous solid nickel solution. The rhenium introduction into the alloy made it possible to substantially increase the temperatures of complete dissolution of the secondary γ' -phase and solidus, expand to 65 °C the existence interval of a single-phase alloy, and significantly narrow the melting interval.

Additions of tantalum and chromium in such a composition no longer lead to positive results (Table 2).

Table 3. The ratio V_T / V_0 at certain temperatures.

$T, ^\circ\text{C}$	Sample №										
	1	2	3	4	5	6	7	8	9	10	11
700	-	-	-	-	-	-	-	-	-	-	-
800	-	0.98	0.96	0.95	0.99	-	-	-	0.98	0.98	0.95
900	0.94	0.90	0.86	0.85	0.90	0.94	0.93	0.97	0.89	0.90	0.85
1000	0.79	0.75	0.71	0.68	0.74	0.79	0.77	0.85	0.74	0.75	0.69
1100	0.56	0.54	0.49	0.45	0.49	0.57	0.53	0.63	0.53	0.52	0.47
1200	0.23	0.25	0.21	0.17	0.17	0.26	0.20	0.32	0.25	0.23	0.19

To assess the thermal stability of a high-temperature nickel alloys Petrushin N.V., Logunov A.V. and Kovalev A.I. [9] proposed a formula relating the volumetric fraction of the γ' -phase at a given temperature V_T with its volume fraction at room temperature V_0 through the ratio of the temperatures of the beginning of dissolution $t_{b.d.}$ and end t_{solv} dissolution of the secondary 'phase:

$$V_T / V_0 = \alpha \cdot [t_{\text{solv}}^2 - t^2] - \mu(t_{\text{solv}} - t_{b.d.}), \quad (1)$$

where $\alpha = (t_{\text{solv}} - t_{b.d.})^{-2}$,

$\mu = 2 \cdot t_{h.d.} / (t_{\text{solv}} - t_{b.d.})^2$,

t – temperature.

A typical dependence of the amount of the secondary γ' -phase on temperature is shown in the Figure 2. The results of the calculations are summarized in Table 3. Calculation analysis shows that

for relatively low-alloyed high-temperature alloys the greatest thermal stability at temperatures below 1100°C is achieved in the base sample (composition 1).

For heavily alloyed high-temperature alloys, the composition with 6 % mass. tantalum (sample 8) has the highest thermal stability at temperatures up to 1200°C. The addition of rhenium to 2% by weight slightly reduces the thermal stability.

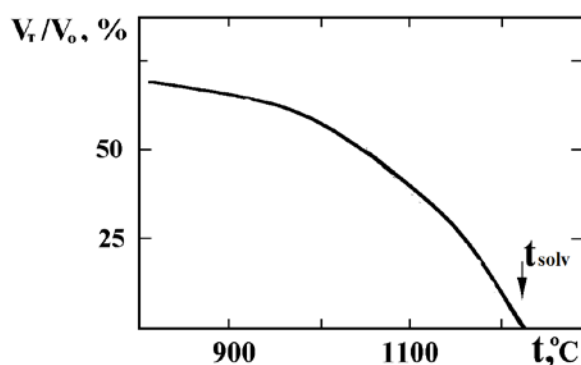


Figure 2. Changing secondary γ' -phase amount in the heat-resistant nickel alloy from the heating temperature.

4. Conclusions

1. New fundamental information has been obtained on the effect of doping on the carbon-free high-temperature nickel alloys phase transformations temperatures. Temperatures for liquidus, solidus, total dissolution of the secondary γ' -phase were determined for all compositions, the melting intervals and the existence of a single-phase nickel solid solution, supercooling of the melt upon cooling were calculated.
2. For relatively low-alloyed carbon-free high-temperature alloys, the greatest positive effect is achieved when they are doped with γ' -forming elements-niobium and titanium.
3. For multicomponent carbon-free high-temperature nickel alloys, compositions containing rhenium and a small amount of tantalum have the most favorable characteristics.
4. The increased content of tungsten, tantalum or chromium in complex-alloyed carbon-free high-temperature nickel alloys leads to a certain decrease in the temperatures of phase transformations.
5. For relatively low-alloyed high-temperature alloys, the maximum thermal stability at temperatures below 1100°C is achieved in the base sample (composition 1). For highly alloyed high-temperature alloys, the composition with 6 % mass. of tantalum has the highest thermal stability at temperatures up to 1200°C.

5. References

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